

A fully *ab initio* quartic force field of spectroscopic quality for SO₃*

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Abstract

The quartic force field of SO₃ was computed fully *ab initio* using coupled cluster (CCSD(T)) methods and basis sets of up to *spdfgh* quality. The effect of inner-shell correlation was taken into account. The addition of tight *d* functions is found to be essential for accurate geometries and harmonic frequencies. The equilibrium geometry and vibrational fundamentals are reproduced to within 0.0003 Å and (on average) 1.15 cm⁻¹, respectively. We recommend the following revised values for the harmonic frequencies: $\omega_1=1082.7$, $\omega_2=502.6$, $\omega_3=1415.4$, $\omega_4=534.0$ cm⁻¹. In addition, we have shown that the addition of inner polarization functions to second-row elements is highly desirable even with more approximate methods like B3LYP, and greatly improves the quality of computed geometries and harmonic frequencies of second-row compounds at negligible extra computational cost. For larger such molecules, the B3LYP/VTZ+1 level of theory should be a very good compromise between accuracy and computational cost.

*In memory of my colleague Dr. Jacqueline Libman OBM (1941–1997)

I. INTRODUCTION

The importance of the sulfuric anhydride (SO_3) molecule in atmospheric and industrial chemistry requires no further elaboration.

Experimental studies of its vibrational spectroscopy have to contend with a number of problems such as the tendency of SO_3 to polymerize, its very hygroscopic character, and its easy decomposition in the gas phase to SO_2 . Possibly this explains why only a relatively small body of rotation-vibration spectroscopy data is available.

The only available anharmonic force field for this prototype planar XY_3 molecule is the work of Dorney, Hoy, and Mills [1] (DHM), who proposed two model force fields. Not enough data are available for an experimental force field refinement.

In recent years, however, the methodology for computing anharmonic force fields fully ab initio has developed to the point where the computed force fields are at least [2,3] suitable starting material for further experimental refinement [4–6] and at best deliver essentially spectroscopic accuracy in their own right [7–10]. (By analogy with Boys’ concept of ‘chemical accuracy’, ± 1 kcal/mol, for energetics, we will arbitrarily define ‘spectroscopic accuracy’ here as ± 1 cm^{-1} on vibrational transition energies.)

Recently, the present author published a calibration study [11] on the anharmonic force field of sulfur dioxide. It was found there that the computed geometry and harmonic frequencies were critically dependent on the presence of high-exponent ‘inner polarization functions’ in the basis set, whose contribution is actually much more important than that of inner-shell correlation. (They also contribute as much as 8 kcal/mol to the total atomization energy of SO_2 [11,12]. This is an extreme version of a phenomenon that appears to occur more generally in second-row compounds [13,14].) Our best computed force field agreed to within 0.0004 Å and 0.03 degrees with experiment for the geometry: the errors in the fundamentals of SO_2 were +3.9, -0.4, and +0.4 cm^{-1} . It would therefore appear that the same level of theory would be sufficient to produce a reliable force field for SO_3 as well.

Some other recent ab initio anharmonic force field calculations on planar XY_3 systems

include the work of Botschwina and coworkers [15] on CF_3 and CF_3^+ , of Schwenke [16] on CH_3 , of Green et al. [17] on SiH_3^+ , of Martin and Lee [18] on BH_3 , and of Pak and Woods [19] on BF_3 and CF_3^+ .

Previous ab initio studies of the vibrational force field were limited to the harmonic part (e.g. [20], which used scaled quantum mechanical (SQM) [21] techniques as well as MCSCF calculations). To the author's knowledge, this paper presents the first accurate anharmonic force field for SO_3 obtained by any method. It will also be shown that the harmonic frequencies derived from experiment by DHM need to be substantially revised.

II. METHODS

All electronic structure calculations were carried out using MOLPRO 96.4 [22] with the `tripu` and `scfpr0` patches [23] installed, or a prerelease version of MOLPRO 97.3 [24] running on a DEC Alpha 500/500 workstation and an SGI Origin 2000 minisupercomputer at the Weizmann Institute of Science.

As in our previous work on SO_2 [11], the CCSD(T) electron correlation method [25,26], as implemented by Hampel *et al.* [27], has been used throughout. The acronym stands for coupled cluster with all single and double substitutions [28] augmented by a quasiperturbative account for triple excitations [25]. From extensive studies (see [29] for a review) this method is known to yield correlation energies very close to the exact n -particle solution within the given basis set as long as the Hartree-Fock determinant is a reasonably good zero-order reference wave function. From the value of the \mathcal{T}_1 diagnostic [30] calculated for SO_3 , 0.018, we see that this condition is definitely fulfilled.

Calculations including only valence correlation were carried out using correlation consistent polarized n -tuple zeta (cc-pVnZ) basis sets of Dunning and coworkers [31,32]. For sulfur/oxygen, the cc-pVTZ and cc-pVQZ basis sets correspond to (15s9p2d1f/10s5p2d1f) and (16s11p3d2f1g/12s6p3d2f1g) primitive sets contracted to [5s4p2d1f/4s3p2d1f] and [6s5p3d2f1g/5s4p3d2f1g], respectively. Because of the strongly polar character of the SO bonds, we have also considered the aug-cc-pVnZ basis sets [33,34], which consist of cc-pVnZ

basis sets with one low-exponent ‘anion’ function added to each angular momentum. In the interest of brevity, the standard acronyms cc-pVnZ and aug'-cc-pVnZ will be replaced by VnZ and AVnZ, respectively.

Furthermore, we considered the addition of a tight d function with exponent $\alpha_D=3.203$ [13] to the sulfur basis set; its presence is indicated by the notation VTZ+1, VQZ+1, and the like.

As in our previous studies on SO and SO₂ [11], H₂SiO [14], and various second-row diatomics [35,13], core correlation was included using the Martin-Taylor basis set [36,37]. This is generated by completely decontracting the cc-pVTZ basis set and adding a single high-exponent p function and two even-tempered series, one of three tight d functions and another of two tight f functions. The exponents are defined as $3^n\alpha$ (rounded to the nearest integer or half-integer), where α represents the highest exponent of that angular momentum already present in the cc-pVTZ basis. Obviously, such a basis set already amply covers the ‘inner polarization’ region as well. For brevity, CCSD(T)/Martin-Taylor calculations with only the valence electrons correlated are denoted CCSD(T)/MTnocore, while in CCSD(T)/MTcore calculations, all orbitals except for the sulfur (1s)-like orbital (which lies too deep to interact appreciably with the valence shell) have been correlated.

Geometry optimizations were carried out by repeated multivariate parabolic interpolation with a step size of 0.001 bohr or radian, and a convergence threshold of about 10^{-5} bohr or radian. Quartic force fields were set up by finite differentiation in symmetry-adapted coordinates

$$S_1 = (r_1 + r_2 + r_3)/\sqrt{3} \quad (1)$$

$$S_2 = \delta \equiv \frac{\vec{r}_1 \cdot \vec{r}_2 \times \vec{r}_3}{r_1 r_2 r_3} \quad (2)$$

$$S_{3a} = (2r_1 - r_2 - r_3)/\sqrt{6} \quad (3)$$

$$S_{3b} = (r_2 - r_3)/\sqrt{2} \quad (4)$$

$$S_{4a} = (2\theta_1 - \theta_2 - \theta_3)/\sqrt{6} \quad (5)$$

$$S_{4b} = (\theta_2 - \theta_3)/\sqrt{2} \quad (6)$$

in which the r_i are the SO bond distances, the θ_i are the OSO bond angles opposite the corresponding r_i , and δ represents the out-of-plane motion. In order to keep higher-order contamination in the quartic portion of the force field to a minimum, fairly small step sizes 0.01 Å and radian were used and CCSD(T) energies converged to essentially machine precision. Generation of the displaced Cartesian geometries and transformation of the internal coordinate force field to Cartesian coordinates were carried out with the help of the INTDER [38] program. The anharmonic spectroscopic analysis was carried out by standard second-order rovibrational perturbation theory using a modified version of SPECTRO [39,40]. No Fermi resonances needed to be accounted for, but some of the rotation-vibration interaction constants needed to be deperturbed for a Coriolis resonance $\omega_2 \approx \omega_4$ around the b axis.

III. RESULTS AND DISCUSSION

Computed and experimentally derived bond distances and harmonic frequencies are given in Table I, while computed and observed fundamentals can be found in Table II.

High-resolution values are available for all fundamentals except ν_1 , for which the Bondybey and English (BE) [41] value of 1068.6 cm⁻¹ appears to be the most reliable one available. ν_3 =1391.5205 cm⁻¹ was taken from the work of Henfrey and Thrush (HT) [42]. The rotational fine structures of the ν_2 and ν_4 bands overlap as well as exhibit Coriolis resonance: Kaldor et al. (KMDM) [43] resolved this spectrum to give ν_2 =497.55 and ν_4 =530.18 cm⁻¹. They also definitively refuted a suggestion by Thomas and Thompson (TT) [44] that the assignments be reversed: the TT band origins (with the correct assignment) are ν_2 =498.5 and ν_4 =529.16 cm⁻¹. A high-resolution study by Ortigoso, Escribano, and Maki (OEM) [45] finally yielded ν_2 =497.5679(1) and ν_4 =530.0863(1) cm⁻¹. In the process, OEM also obtained improved values of the ground state rotational constants, and particularly a revised r_e =1.41732 Å, which is near the lower limit of the earlier DHM value, r_e =1.4184±0.0010 Å.

Comparing the observed with the calculated fundamentals, it is immediately seen that the CCSD(T)/VTZ fundamentals leave a lot to be desired: errors with respect to the experimental values (BE,OEM,HT) are -25.1, -15.5, -20.4, and -16.1 cm⁻¹, respectively, for

ν_1 , ν_2 , ν_3 , and ν_4 . Switching to a VTZ+1 basis set (i.e. adding the tight d function on S) dramatically cuts these errors to -1.6, +1.0, +4.8, and -2.0 cm^{-1} .

Turning to Table I, we see that in addition $r(\text{SO})$ is shortened by no less than 0.0116 Å, thus cutting the discrepancy with experiment by more than half. Actually, the tight d function appears to be even more important for the quality of the results than increasing the basis set from VTZ to VQZ. Adding the inner polarization function to the VQZ basis set has a smaller effect than for the VTZ basis set (as it well should, since the VQZ basis set contains tighter d functions than its VTZ counterpart), but still affects the bond length by -0.0050 Å. The main difference between the VTZ+1 and VQZ+1 harmonics is that ω_3 drops by about 4.5 cm^{-1} , removing the largest error remaining in the fundamentals at the CCSD(T)/VTZ+1 level.

Given the strongly polar character of the S-O bonds in SO_3 , the addition of anion functions is expected to have a nontrivial effect. From VTZ+1 to AVTZ+1, the harmonics are lowered by no less than -13.2, -5.7, -20.1, and -8.0 cm^{-1} , respectively; from VQZ+1 to AVQZ+1, the effect is much weaker: -3.6, -2.4, -6.0, and -2.4 cm^{-1} . While the addition of diffuse functions lengthens $r(\text{SO})$ by +0.0030 Å between VTZ+1 and AVTZ+1, this likewise becomes much less significant from VQZ+1 to AVQZ+1 (+0.0009 Å).

Computing anharmonic corrections with these large basis sets for a four-heavy atom molecule is beyond the presently available computational resources. However, it is seen here that even from CCSD(T)/VTZ to CCSD(T)/VTZ+1, the basis set effect on the anharmonic corrections is very modest (-0.10, -0.27, -0.07, and +0.01 cm^{-1}), while for SO_2 [11], their basis set dependence was likewise found to be quite mild. We therefore opt for the CCSD(T)/VTZ+1 anharmonicities and will merely substitute an improved bond distance and improved harmonic frequencies in the analysis.

Doing the latter with the CCSD(T)/AVQZ+1 data yields harmonic frequencies which are systematically too low, with r_e of course still being 0.0053 Å longer than experiment.

A complete CCSD(T)/MTcore harmonic frequency calculation proved too demanding in terms of computational resources: what could be successfully completed was a univariate

optimization of r_e , with ω_1 being obtained as a by-product. The CCSD(T)/MTcore r_e falls within the error bar of the DHM value and is just 0.00032 Å longer than the OEM value. The contributions of inner-shell correlation to r_e and ω_1 turn out to be much more modest (-0.00283 Å, $+4.2$ cm $^{-1}$) than those of inner polarization.

If we consider the ratios $\omega_i(\text{MTcore})/\omega_i(\text{MTnocode})$ for ω_1 and for the harmonic frequencies of SO $_2$, we find that these ratios are remarkably similar: 1.0039, 1.0037, 1.0038, and 1.0036. (They correspond almost exactly to $[r_e(\text{MTcore})/r_e(\text{MTnocode})]^2$.) Under these circumstances, we might be able to obtain ‘best estimate’ harmonic frequencies by scaling the CCSD(T)/AVQZ+1 values by $\omega_1(\text{MTcore})/\omega_1(\text{MTnocode}) = 1.00386$, which leads to the following values: 1081.2, 503.1, 1415.1, and 531.6 cm $^{-1}$.

We now substitute these harmonic frequencies and the CCSD(T)/MTcore geometry in the spectroscopic analysis, and thus obtain the fundamentals labeled ‘best’ in Table II. Compared to the (BE,OEM,HT) set of experimental values, the remaining discrepancies are -1.5, +0.4, -0.3, and -2.4 cm $^{-1}$, or 1.15 cm $^{-1}$ on average. We can thus safely claim ‘spectroscopic accuracy’ for our best force field.

Turning now to the rotational constants (Table III), we see that the computed and experimentally derived (OEM) B_e agree to -0.02 %: C_e brings no additional information since it is fixed by the planarity relation $C_e = B_e/2$. From our computed rotational constants we can however now determine computed B_0 and C_0 , which likewise turn out to be in excellent agreement with the observed values: -0.06 % and -0.03 %, respectively. (B_0 and C_0 are independent data because of the inertial defect.) The fact that the rotational constants are consistently computed slightly too small is consistent with our bond distance being slightly longer than the true value. From the relationship (in this case) $r_0 = r_e\sqrt{B_e/B_0}$, we find $r_0(\text{calc.})=1.42004$ Å, compared to an experimental [46] value $r_0(\text{obs.})=1.4198\pm0.0002$ Å, and one derived from the OEM B_0 of 1.41963 Å. The discrepancy of +0.0004 Å between the computed and OEM-derived r_0 is consistent with the discrepancy of +0.0003 Å between the computed and OEM r_e values. Aside from the observation that this would be considered excellent agreement between theory and experiment by any reasonable standard, this sug-

gests that the OEM equilibrium bond distance of 1.41732 Å would be accurate to 0.0001 Å or better. The computed r_g (electron diffraction) distance from our force field, 1.42275 Å, is substantially longer than the experimental electron diffraction result [47], 1.4188 ± 0.003 Å. Since this latter study also finds an unrealistically short $r_e = 1.414_2$ and $r_z = 1.416_9$ Å (our own computed $r_z = 1.42143$ Å), we can safely conclude that the electron diffraction result is in error. (For a review of the different types of bond distances discussed, see Ref. [48].)

Our best harmonic frequencies agree relatively well with those obtained by DHM from the experimental fundamentals and a valence model for anharmonicity, except for ω_1 which still is about 16 cm^{-1} too low in the better of their two models. (The discrepancies for ω_3 and ω_4 are still substantially bigger than the differences between the computed and observed fundamentals, and it can safely be stated that the present ab initio values are considerably more reliable than the experimentally derived ones.) It thus comes as no surprise that the anharmonicity constants (Table IV) obtained by DHM from their valence models (particularly $\omega_1 - \nu_1$, which has the wrong sign) differ profoundly from the presently computed set, which clearly is the more reliable one.

A set of ‘experimental’ harmonic frequencies can be derived from our best force field and the observed fundamentals by iteratively substituting $\omega_i^{[n+1]} = \omega_i^{[n]} + \nu_i^{[\text{expt.}]} - \nu_i^{[n]}$ in the spectroscopic analysis. The values thus obtained are given as the entry labeled ‘Recommended’ in Table I.

Coriolis and rotation-vibration coupling constants can be found in Table IV. The computed Coriolis coupling constant $B_e \zeta_{24}^B$ is found as 0.1764 cm^{-1} from our best force field, which agrees reasonably, but not very, well with the OEM ‘Fit I’ value of $0.191694(460) \text{ cm}^{-1}$. They note that their fit exhibits very strong dependency between $B_e \zeta_{24}^B$ and such parameters as the rotational l -doubling constant q_4 and the rovibrational coupling constants α_{2B} and α_{4B} . Upon constraining $B_e \zeta_{24}^B$ to the force-field derived value of 0.1801, they found (Fit II in their paper) that all the abovementioned constants change drastically. It is noteworthy that our computed $\alpha_{2B} = 0.00031$, $\alpha_{4B} = -0.00050$, and $q_4 = 0.00063 \text{ cm}^{-1}$ agree *much* better with the ‘Fit II’ values of 0.000150, -0.000404, and 0.000497 cm^{-1} , respectively, than

with the ‘Fit I’ values of -0.000381, -0.000140, and -0.000047 cm^{-1} , respectively. Linear extrapolation suggests that much of the residual discrepancies between our computed and the ‘Fit II’ would disappear if our $B_e\zeta_{24}^B$ value had been substituted in the experimental analysis.

OEM also obtained α_{2C} and α_{4C} values, which are in excellent agreement with our calculations, as are the α_{3B} and α_{3C} values of HT. Our computed α_{1B} and α_{1C} are larger than the model-derived values of DHM, which appear to be on the low side for all other constants as well. The centrifugal distortion constants are quite small, and agree with the experimental values of OEM to within the latter’s uncertainties.

The trends in the computed quadratic force constants (Table V) closely parallel those in the harmonic frequencies. (The most striking difference with the DHM quadratic force constants, which reproduce the fundamentals rather than either of their sets of harmonic frequencies, lies in the stretch-bend coupling constant F_{34} .)

In order to stimulate further research on the vibrational spectrum of SO_3 , the symmetry-unique cubic and quartic force constants in symmetry coordinates have been made available in Table VI. The force fields in Cartesian, symmetry, and normal coordinates can also be downloaded in machine-readable form on the World Wide Web at the Uniform Resource Locator (URL) <http://theochem.weizmann.ac.il/web/Papers/so3.html>

IV. A NOTE ON LOWER-LEVEL CALCULATIONS

Some readers might wonder how well less computationally intensive methods would do for the mechanical properties of SO_3 and the other sulfur oxides, and whether the presence of the tight d functions is still relevant at that accuracy level.

In order to answer these questions, we have carried out geometry optimizations and harmonic frequency calculations for SO , SO_2 , and SO_3 using the popular B3LYP density functional method [49,50] as implemented in GAUSSIAN 94 [51]. The VTZ, VTZ+1, and AVTZ+1 basis sets were considered, as was the popular 6-31+G* basis set. The results are summarized in Table VII.

It is immediately seen that the 6-31+G* basis set systematically overestimates bond

lengths by no less than 0.035 Å, and (largely as a result thereof) underestimates stretching frequencies by as much as 80 cm⁻¹ and the SO₃ out-of-plane bending frequency by about 50 cm⁻¹. These errors are substantially reduced by using the VTZ basis set. However, at very small additional expense, the addition of a tight *d* function on S leads to quite respectable agreement with experiment: residual errors for the B3LYP/VTZ+1 harmonic frequencies are +5.7 cm⁻¹ in SO, {+0.4,+16.2,+6.5} cm⁻¹ in SO₂, and {-5.7,-8.4,-10.5,-6.4} cm⁻¹ in SO₃. Trends in the effect of the tight *d* function closely parallel those seen at the CCSD(T) level, which is not surprising since it is essentially an SCF rather than a dynamical correlation effect. [11,13]

At the B3LYP/VTZ+1 level, all bond lengths are now within +0.006–0.008 Å of experiment, and the OSO angle is in excellent agreement with experiment. Overall, performance with the VTZ+1 basis set is as good as we can reasonably hope to get (e.g. [52]) at the B3LYP level.

It is therefore clear that the addition of tight *d* functions to the basis set is eminently worthwhile even for less than ‘benchmark quality’ calculations on second-row compounds, as well as that B3LYP/VTZ+1 would represent an excellent compromise between accuracy and computational cost for geometry and frequency calculations on larger second-row systems.

V. CONCLUSIONS

The first-ever accurate anharmonic force field for SO₃ has been obtained fully *ab initio*. We have been able to establish that:

- r_e is reproduced to within +0.0003 Å, and the fundamentals to within 1.15 cm⁻¹, on average;
- like for SO₂ and (to a lesser extent) for second-row compounds in general, the addition of tight *d* functions (‘inner polarization functions’) to the basis set is essential for accurate results;

- the following revised values are recommended values for the harmonic frequencies:
 $\omega_1=1082.7$, $\omega_2=502.6$, $\omega_3=1415.4$, $\omega_4=534.0$ cm^{-1} ;
- our computed rovibrational coupling, rotational l -doubling, and Coriolis coupling constants suggest a preference for the set of constants in ‘Fit II’ in Ref. [45] (OEM) over those in ‘Fit I’.

In addition, we have shown that the addition of inner polarization functions to second-row elements is highly desirable even with more approximate methods like B3LYP, and greatly improves the quality of computed geometries and harmonic frequencies of second-row compounds at negligible extra computational cost. For larger such molecules, the B3LYP/VTZ+1 level of theory should be a very good compromise between expense and accuracy.

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TABLES

TABLE I. Equilibrium bond distance (\AA) and harmonic frequencies (cm^{-1}) of SO_3

	r_e	$\omega_1(a'_1)$	$\omega_2(a''_2)$	$\omega_3(e')$	$\omega_4(e')$
CCSD(T)/VTZ	1.43753	1057.7	487.5	1395.1	518.1
CCSD(T)/VTZ+1	1.42594	1081.1	503.6	1420.2	532.0
CCSD(T)/VQZ	1.42780	1071.1	496.2	1405.6	526.8
CCSD(T)/VQZ+1	1.42279	1080.6	503.6	1415.7	532.0
CCSD(T)/AVTZ	1.44038	1043.9	482.4	1374.1	509.7
CCSD(T)/AVTZ+1	1.42890	1067.9	497.9	1400.1	524.0
CCSD(T)/AVQZ+1	1.42372	1077.0	501.2	1409.7	529.6
CCSD(T)/MTcore	1.41764	1092.5	—	—	—
CCSD(T)/MTnocode	1.42047	1088.3	—	—	—
Best estimate ^a	1.41764	1081.2	503.1	1415.1	531.6
Experiment	1.41732 [45], 1.4184 [1]				
‘VF’ model (DHM) [1]		1048.08	503.81	1408.96	538.64
‘Extended’ model (DHM) [1]		1064.89	505.97	1410.00	535.62
Recommended ^b		1082.7	502.6	1415.4	534.0

(a) harmonics obtained by scaling CCSD(T)/AVQZ+1 values with ratio of 1.00386 between CCSD(T)/MTcore and CCSD(T)/MTnocode value for ω_1 (see text)

(b) this work. Obtained by iteration of harmonics with best computed force field to exactly reproduce experimental fundamentals.

TABLE II. Anharmonic corrections (cm^{-1}) and fundamentals (cm^{-1}) for SO_3

	$\omega_1 - \nu_1$	$\omega_2 - \nu_2$	$\omega_3 - \nu_3$	$\omega_4 - \nu_4$
CCSD(T)/VTZ	14.182	5.342	23.989	3.911
CCSD(T)/VTZ+1	14.083	5.067	23.921	3.920
Best estimate ^a	14.143	5.069	23.930	3.921
‘VF’ model (DHM)	−19.9	6.3	19.1	8.5
‘Extended’ model(DHM)	−3.1	8.4	20.1	5.4
	ν_1	ν_2	ν_3	ν_4
VTZ	1043.5	482.1	1371.1	514.0
VTZ+1	1067.0	498.6	1396.3	528.1
Best calc. ^a	1067.1	498.0	1391.2	527.7
Expt.	1068.6 ^b	497.5679(1) ^c	1391.5205 ^d	530.0863(1) ^c

(a) from substituting CCSD(T)/MTcore geometry and ‘best estimate’ harmonic frequencies in spectroscopic analysis of CCSD(T)/VTZ+1 force field

(b) Ref. [41] (BE)

(c) Ref. [45] (OEM)

(d) Ref. [42] (HT)

TABLE III. Computed and observed bond distances (\AA), rotational constants (cm^{-1}), and centrifugal distortion constants (cm^{-1}) of SO_3

	Best calc.	Expt.
r_e	1.41764	1.41732^a , 1.4184 ± 0.0010^b , 1.4142^c
r_0	1.42004	1.4198 ± 0.0002^d , 1.41963^e
r_g	1.42275	1.4188 ± 0.003^c
r_z	1.42143	1.4169^c
B_e	0.34962	0.34968^a , 0.34923^b
C_e	0.17481	$B_e/2$
B_0	0.34844	0.3485439^a , 0.34857^b
C_0	0.17393	0.173984^a , 0.17402^b
$10^7 D_J$	3.092	$3.096(8)^a$
$10^7 D_{JK}$	-5.452	$-5.47(2)^a$
$10^7 D_K$	2.543	2.55^f

(a) Ref. [45] (OEM)

(b) Ref. [1] (DHM)

(c) Ref. [47]

(d) Kaldor and Maki [43]

(e) From B_0 of OEM

(f) from planarity relation $D_K = -(2D_J + 3D_{JK})/4$

TABLE IV. Anharmonicity constants, rotation-vibration coupling constants, and rotational l -doubling constants of SO_3 . All values are in cm^{-1} . Constants marked with an asterisk have been deperturbed for Coriolis resonance

	Best calc. (this work)	‘VF’ model DHM	‘Extended’ model DHM	Experiment OEM
α_{1B}	0.00081	0.00067	0.00067	
α_{2B}	0.00468	0.00402	0.00425	
α_{2B}^*	0.00031			-0.000381 ^a , 0.000150 ^b
α_{3B}	0.00111	0.00103	0.00103	0.001132(1) ^c
α_{4B}	-0.00268	-0.00271	-0.00269	
α_{4B}^*	-0.00050			-0.000140 ^a , -0.000404 ^b
α_{1C}	0.00041	0.00033	0.00033	
α_{2C}	-0.00013	-0.00026	-0.00019	-0.000130 ^d
α_{3C}	0.00058	0.00054	0.00054	0.0005999(3) ^c
α_{4C}	0.00015	0.00005	0.00008	0.000157 ^d
q_3	-0.00012	0.00002	0.00002	
q_4	0.00500	0.00345	0.00345	
q_4^*	0.00063			-0.000047 ^a , 0.000483 ^b
$B\zeta_{24}$	0.1764			0.1917(5) ^a , 0.1801 ^b
X_{11}	-2.031	-1.37	-1.38	
X_{12}	1.113	10.86	5.08	
X_{13}	-9.388	-7.02	-6.94	
X_{14}	-1.249	24.27	10.27	
X_{22}	-0.748	-4.24	-3.21	
X_{23}	-4.403	-1.22	-2.36	
X_{24}	0.284	-1.98	-2.18	
X_{33}	-5.434	-4.66	-4.63	
X_{34}	-3.553	1.00	-1.60	
X_{44}	-0.011	-6.20	-2.63	
G_{33}	2.828	2.46	2.47	
G_{34}	-0.279	-0.20	-0.18	
G_{44}	0.150	6.25	2.08	
R_{44}	2.528	—	—	

(a) Ref. [45] (OEM), Fit I.

(b) OEM, Fit II ($B\zeta_{24}$ constrained to force field value 0.1801 cm^{-1}).

(c) Ref. [42] (HT)

(d) Ref. [45] (OEM)

TABLE V. Quadratic force constants for SO_3 in symmetry-adapted internal coordinates. Units are aJ, Å, and radian, and the restricted summation convention is used.

	F_{11}	F_{22}	F_{33}	F_{34}	F_{44}
DHM [1] ^a	5.374	0.309	5.269	-0.460	0.617
CCSD(T)/VTZ	5.27167	0.30839	5.24224	-0.33254	0.61456
CCSD(T)/VTZ+1	5.50748	0.32393	5.44096	-0.36341	0.63755
CCSD(T)/AVTZ	5.13533	0.30320	5.08914	-0.33047	0.59721
CCSD(T)/AVTZ+1	5.37410	0.31787	5.29261	-0.36336	0.62080
CCSD(T)/VQZ	5.40597	0.31526	5.32635	-0.35288	0.62686
CCSD(T)/VQZ+1	5.50201	0.32249	5.40691	-0.36436	0.63458
CCSD(T)/AVQZ+1	5.46613	0.31990	5.36281	-0.36459	0.62976
CCSD(T)/MTcore	5.62424				
CCSD(T)/MTnocore	5.58098				

(a) reproduce older values of fundamentals, *not* harmonic frequencies

TABLE VI. Computed cubic and quartic force constants for SO_3 in symmetry-adapted internal coordinates. Units are aJ, Å, and radian, and the restricted summation convention is used.

	CCSD(T)/VTZ	CCSD(T)/VTZ+1
F_{111}	-7.31818	-7.62772
F_{122}	-0.58764	-0.60070
$F_{13a3a} = F_{13b3b}$	-20.91209	-21.57875
$F_{14a4a} = F_{14b4b}$	-0.98244	-1.01975
$F_{13a4a} = F_{13b4b}$	1.02568	1.05182
$F_{3a3a3a} = -F_{3a3b3b}/3$	-4.84233	-4.99590
$F_{3a3a4a} = -F_{3a3b4b}/2 = -F_{3b3b4a}$	-0.29699	-0.32604
$F_{3a4a4a} = -F_{3a4b4b} = -F_{3b4b4a}/2$	0.37460	0.38143
$F_{4a4a4a} = -F_{4a4b4b}/3$	-0.15162	-0.15666
F_{1111}	6.05065	6.12886
F_{1122}	0.40348	0.39441
F_{2222}	0.06145	0.06940
$F_{113a3a} = F_{113b3b}$	33.41738	33.72571
$F_{113a4a} = F_{113b4b}$	-1.13882	-1.10147
$F_{114a4a} = F_{114b4b}$	0.68428	0.71380
$F_{223a3a} = F_{223b3b}$	-0.29300	-0.30274
$F_{223a4a} = F_{223b4b}$	-0.34408	-0.36252
$F_{224a4a} = F_{224b4b}$	0.26088	0.27144
$F_{13a3a3a} = -F_{13a3b3b}/3$	15.54250	15.63856
$F_{13a3a4a} = -F_{13b3b4a} = -F_{13a3b4b}/2$	0.70144	0.78582
$F_{13a4a4a} = -F_{13a4b4b} = -F_{13b4b4a}/2$	-0.39367	-0.47240
$F_{14a4a4a} = -F_{14a4b4b}/3$	0.25712	0.26586
$F_{3a3a3a3a} = F_{3a3a3b3b}/2 = F_{3b3b3b3b}$	8.41884	8.50409
$F_{3a3a3a4a} = F_{3a3b3b4a} = F_{3a3a3b4b} = F_{3b3b3b4b}$	0.04720	0.08160
$F_{3a3a4a4a} = F_{3b3b4b4b}$	0.22378	0.21243
$F_{3a3a4b4b} = F_{3b3b4a4a}$	-0.36425	-0.40564
$F_{3a3b4a4b} = 2(F_{3a3a4a4a} - F_{3a3a4b4b})$		
$F_{3a4a4a4a} = F_{3b4b4a4a} = F_{3a4a4b4b} = F_{3b4b4b4b}$	-0.27446	-0.29029
$F_{4a4a4a4a} = F_{4a4a4b4b}/2 = F_{4b4b4b4b}$	0.12569	0.12956

TABLE VII. Basis set convergence for geometries (\AA , degrees) and harmonic frequencies (cm^{-1}) of SO_n ($n=1-3$) at the B3LYP level

		6-31+G*	VTZ	VTZ+1	AVTZ+1	Experiment
SO	r_e	1.5157	1.4998	1.4891	1.4888	1.48108 [53]
	ω_e	1118.3	1146.6	1157.4	1156.2	1150.695(8) [53]
SO ₂	r_e	1.4655	1.4504	1.4367	1.4380	1.43076(13) [54]
	θ_e	118.68	118.31	119.25	119.16	119.33(1) [54]
	ω_1	1133.0	1164.7	1184.1	1177.8	1167.91(4) [55]
	ω_2	498.4	516.5	522.6	519.6	522.21(3) [55]
	ω_3	1315.9	1352.1	1388.3	1376.2	1381.82(2) [55]
SO ₃	r_e	1.4543	1.4389	1.4259	1.4270	1.41732 [45]
	ω_1	1018.1	1051.2	1077.0	1071.4	1082.7 ^a
	ω_2	452.9	476.3	494.2	492.2	502.6 ^a
	ω_3	1334.7	1375.3	1404.9	1394.1	1415.4 ^a
	ω_4	492.5	512.2	527.6	523.8	534.0 ^a

(a) Recommended values (this work).